

- 1 -

Novel holographic recording material

The present invention relates to a recording material for a holographic volume storage medium, its preparation and use for the recording of volume holograms.

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Holography is a method in which, using the interference between two coherent light beams (signal wave and reference wave), objects can be imaged in suitable storage materials and those images can be read out again using light (reading beam) (D. Gabor, Nature 151, 454 (1948), N. H. Farath, Advances in Holography, Vol. 3, Marcel Decker (1977), H. M. Smith, Holographic Recording Materials, Springer (1977)). By changing the angle between the signal wave and the reference wave on the one hand and the holographic storage material on the other hand, numerous holograms can be written into the material at one and the same specimen position and ultimately can also be read out again individually. The coherent light source used is generally the light of a laser. A very wide variety of materials are described as the storage material, for example inorganic crystals such as LiNbO₃ (for example), organic polymers (for example M. Eich, J. H. Wendorff, Makromol. Chem., Rapid Commun. 8, 467 (1987), J. H. Wendorff, M. Eich, Mol. Cryst. Liq. Cryst. 169, 133 (1989)) or photopolymers (Uh-Sock Rhee *et al.*, Applied Optics, 34 (5), 846 (1995)).

20

However, those materials do not yet meet all the requirements made of a holographic recording medium. In particular, the recorded hologram does not have adequate stability. Multiple recording is generally possible to only a limited extent, since on recording a new hologram, the hologram already recorded is overwritten and therefore erased. That is true especially of inorganic crystals, which are subjected to complex heat treatment in order to compensate for those stability problems. Photopolymers, on the other hand, exhibit the problem of shrinkage, which has an adverse effect on the holographic imaging properties.

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- 2 -

Materials having a high degree of stability of the recorded holograms are also known, for example from EP 0 704 513 (LeA 30655) and German Application DE-A-19703132 (LeA 31821), which has not yet been laid open.

5 However, the high optical density of those materials does not permit the preparation of holographic volume storage media such as are required for the storage of numerous holograms in a storage material.

10 Accordingly, there was a need for a material which is suitable for the preparation of sufficiently thick holographic volume storage media and which allows numerous holograms to be stored at one specimen position of the recording material in such a manner that they have long-term stability. With the materials known hitherto, the storage of numerous holograms one after another at one position led to the gradual erasing of the holographically stored information: holograms recorded later
15 addressed the same molecules as had been used in the building up of holograms recorded previously, so that the information of earlier holograms was lost after only a few further recording processes.

20 Accordingly, the invention provides a recording material for a holographic volume storage medium, containing at least one dye which changes its spatial arrangement when a hologram is recorded and, optionally, at least one shape-anisotropic grouping, characterised in that it permits the recording of two or more holograms at one specimen position.

25 That is preferably effected in that the dye, of which there is at least one, changes its spatial arrangement in such a manner that it can no longer be excited by the electromagnetic radiation, or changes its absorption behaviour, in particular lowers its sensitivity to the actinic light, preferably reduces it by from 10 % to 100 %, more preferably from 50 % to 100 % and most preferably from 90 % to 100 %, in each
30 case based on the sensitivity prior to recording of the first hologram.

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- 3 -

However, the dye can also reduce its absorption behaviour, in particular its sensitivity to the actinic light, in that it flips into the direction perpendicular to the polarising direction of the actinic light and its molecular longitudinal axis comes to lie at an angle with the polarising direction of the actinic light of from 10° to 90°, preferably from 50° to 90°, more preferably from 75° to 90° and most preferably from 85° to 90°.

In that manner it is possible successfully to carry out the recording of several holograms at one specimen position, that is to say the information of the early holograms is not erased completely.

That change in excitation behaviour with respect to electromagnetic radiation when the hologram is recorded can be achieved by the dye changing its spatial arrangement in the polymeric or oligomeric organic, amorphous material.

With materials of that type it is possible, when a hologram is recorded, to prevent the holograms-already previously recorded in that material from being unacceptably diminished, completely damaged or even entirely overwritten.

From the point of view of measurement techniques, an unacceptable attenuation means that the remaining information can no longer be resolved in relation to the background noise.

The information is stored holographically. To that end, two polarised, coherent beams are brought to interference on the specimen.

As a result of exposure to that actinic light, the dyes change their spatial position in the polymeric or oligomeric layers. Dyes which, on exposure, orient their molecular longitudinal axis into the plane spanned by the two recording beams (incident plane)

can no longer be excited by that light if the polarisation of the light lies perpendicular to the incident plane. The information (hologram) recorded in those dyes during that recording process is protected against change during recording of a subsequent hologram. Dyes which do not come to lie completely perpendicularly to the polarising direction of the light but form an angle Θ other than 90° with that polarising direction, are addressed further during subsequent hologram exposures. However, the probability of those dyes being reoriented and, especially, the light sensitivity of the dyes decrease all the more, the closer the angle of the molecular longitudinal axis to the 90° position.

The molecular longitudinal axis can be determined, for example, by means of the molecular form by molecular modelling (e.g. CERIUSt²).

The reorientation of the dyes after exposure to actinic light results, for example, from investigations into polarised absorption spectroscopy: A sample previously exposed to actinic light is studied between two polarisers in a UV/VIS spectrometer (e.g. CARY 4G, UV/VIS spectrometer) in the spectral range of the absorption of the dyes. When the sample is rotated about the sample normal, and with the polarisers in a suitable position, for example in the crossed condition, the reorientation of the dyes follows from the variation in intensity of the extinction as a function of the sample angle and as a result can be clearly determined.

For the recording of several holograms there are various multiplex processes, such as angle multiplexing, wavelength multiplexing, phase multiplexing, shift multiplexing, peristrophic multiplexing and others.

A measure of the sensitivity to the actinic light is the holographic sensitivity. It is calculated, for example, from the holographic growth curve, that is to say the development of the diffraction efficiency (= diffracted intensity based on incident intensity of the reading laser) as a function of the energy deposited by the recording

beams. The sensitivity is defined as the gradient of the root of the diffraction efficiency according to the deposited energy, standardised to the thickness of the storage medium.

- 5 The invention provides a recording material for a holographic volume storage medium, which at the wavelength of the recording laser has an optical density ≤ 2 , preferably ≤ 1 , more preferably ≤ 0.3 . In that manner it is possible to ensure that the actinic light leads to homogeneous transillumination of the entire storage medium and a thick hologram can be produced. The optical density can be determined using commercial UV/VIS spectrometers (e.g. CARY, 4G, UV/VIS spectrometer).
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The recording material according to the invention is preferably a material which has an irradiated thickness of ≥ 0.1 mm, more preferably 0.5 mm, more preferably still ≥ 1 mm and most preferably not greater than 5 cm.

- 15 The grouping that interacts with the electromagnetic radiation is a dye. The material according to the invention consequently contains at least one dye. The electromagnetic radiation is preferably laser light, preferably in the wavelength range from 390 to 800 nm, more preferably in the range from 400 to 650 nm, most preferably in the range from 510 to 570 nm.
- 20

For the purposes of reading, the recording material is not exposed to two interfering beams, as in the case of recording, but only to one beam, the reading beam.

- 25 The wavelength of the reading beam is preferably of longer wavelength than that of the signal wave and the reference wave, for example from 70 to 500 nm longer. However, reading with the wavelength of the recording laser is also possible and will be used especially in the case of the commercial use of holographic volume storage media. For that purpose, however, the energy of the reading beam is reduced

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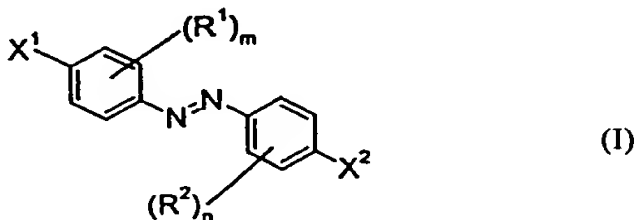
during the reading process either by reducing the intensity of exposure or the exposure time, or by reducing the intensity of exposure and the exposure time.

The optical density of the recording material according to the invention is adjusted
5 by the following two parameters

- a) *via* the molar extinction coefficient of the dye, of which there is at least one, and/or
- b) *via* the concentration of the dye, of which there is at least one, in the polymeric
10 or oligomeric organic material.

Dyes having low extinction coefficients are, for example, dyes having a non-polar and/or only slightly polarisable structure. Such dyes may originate, for example, from the classes of the anthraquinone, stilbene, azastilbene, azo or methine dyes. Azo dyes are preferred. Special preference is given to azo dyes having an absorption
15 maximum of the $\pi\pi^*$ band that is less than or equal to 400 nm, more preferably less than 400 nm.

Azo dyes have, for example, the following structure of formula (I).



wherein

R¹ and R² each independently of the other represents hydrogen or a non-ionic
substituent, and

- 7 -

R¹ may additionally represent -X^{1'}-R³,

m and n each independently of the other represents an integer from 0 to 4, preferably from 0 to 2.

X¹ and X² represent -X^{1'}-R³ and X^{2'}-R⁴, respectively,

X^{1'} and X^{2'} represent a direct bond, -O-, -S-, -(N-R⁵)-, -C(R⁶R⁷)-, -(C=O)-, -(CO-O)-, -(CO-NR⁵)-, -(SO₂)-, -(SO₂-O)-, -(SO₂-NR⁵)-, -(C=NR⁸)- or -(CNR⁸-NR⁵)-,

R³, R⁴, R⁵ and R⁸ each independently of the others represents hydrogen, C₁- to C₂₀-alkyl, C₃- to C₁₀-cycloalkyl, C₂- to C₂₀-alkenyl, C₆- to C₁₀-aryl, C₁- to C₂₀-alkyl-(C=O)-, C₃- to C₁₀-cycloalkyl-(C=O)-, C₂- to C₂₀-alkenyl-(C=O)-, C₆- to C₁₀-aryl-(C=O)-, C₁- to C₂₀-alkyl-(SO₂)-, C₃- to C₁₀-cycloalkyl-(SO₂)-, C₂- to C₂₀-alkenyl-(SO₂)- or C₆- to C₁₀-aryl-(SO₂)-, or

X^{1'}-R³ and X^{2'}-R⁴ may represent hydrogen, halogen, cyano, nitro, CF₃ or CCl₃,

R⁶ and R⁷ each independently of the other represents hydrogen, halogen, C₁- to C₂₀-alkyl, C₁- to C₂₀-alkoxy, C₃- to C₁₀-cycloalkyl, C₂- to C₂₀-alkenyl or C₆- to C₁₀-aryl.

Non-ionic substituents are to be understood as being halogen, cyano, nitro, C₁- to C₂₀-alkyl, C₁- to C₂₀-alkoxy, phenoxy, C₃- to C₁₀-cycloalkyl, C₂- to C₂₀-alkenyl or C₆- to C₁₀-aryl, C₁- to C₂₀-alkyl-(C=O)-, C₆- to C₁₀-aryl-(C=O)-, C₁- to C₂₀-alkyl-(SO₂)-, C₁- to C₂₀-alkyl-(C=O)-O-, C₁- to C₂₀-alkyl-(C=O)-NH-, C₆- to C₁₀-aryl-(C=O)-NH-, C₁- to C₂₀-alkyl-O-(C=O)-, C₁- to C₂₀-alkyl-NH-(C=O)- or C₆- to C₁₀-aryl-NH-(C=O)-.

5 The alkyl, cycloalkyl, alkenyl and aryl radicals may in turn be substituted by up to three radicals from the group halogen, cyano, nitro, C₁- to C₂₀-alkyl, C₁- to C₂₀-alkoxy, C₃- to C₁₀-cycloalkyl, C₂- to C₂₀-alkenyl or C₆- to C₁₀-aryl, and the alkyl and alkenyl radicals may be straight-chained or branched.

Halogen is to be understood as being fluorine, chlorine, bromine and iodine, particularly fluorine and chlorine.

10 The recording material according to the invention is preferably polymeric or oligomeric organic, amorphous material, particularly preferably a side-chain polymer, also particularly preferably a block copolymer and/or a graft polymer.

15 The principal chains of the side-chain polymer originate from the following basic structures: polyacrylate, polymethacrylate, polysiloxane, polyurea, polyurethane, polyester or cellulose. Polyacrylate and polymethacrylate are preferred.

20 The block copolymers consist of a plurality of blocks, of which at least one type contains the above-described copolymer systems. The other blocks consist of non-functionalised polymer structures which serve to dilute the functional block in order to adjust the required optical density. The extent of the functional block is below the wavelength of light, preferably in the region of less than 200 nm, more preferably less than 100 nm.

25 The polymerisation of the block copolymers takes place, for example, by means of free-radical or anionic polymerisation or by means of other suitable polymerisation processes, optionally followed by a polymer-analogous reaction, or by a combination of those methods. The homogeneity of the systems is in a range less than 2.0, preferably less than 1.5. The molecular weight of the block copolymers

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- 9 -

obtained by free-radical polymerisation reaches values in the region of 50,000; values greater than 100,000 can be adjusted by anionic polymerisation.

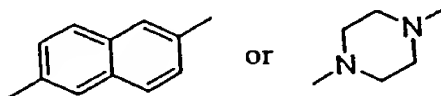
The dyes, especially the azo dyes of formula (I), are bonded to those polymer structures covalently, generally by way of a spacer. For example, X¹ (or X² or R¹) then represents such a spacer, especially in the meaning X¹-(Q¹)_i-T¹-S¹-

wherein

10 X¹ is as defined above,

Q¹ represents -O-, -S-, -(N-R⁵)-, -C(R⁶R⁷)-, -(C=O)-, -(CO-O)-, -(CO-NR⁵)-, -(SO₂)-, -(SO₂-O)-, -(SO₂-NR⁵)-, -(C=NR⁸)-, -(CNR⁸-NR⁵)-, -(CH₂)_p-, p- or m-C₆H₄- or a divalent radical of the formula

15



20 i represents an integer from 0 to 4, wherein when i > 1 the individual radicals Q¹ may have different meanings,

T¹ represents -(CH₂)_p-, wherein the chain may be interrupted by -O-, -NR⁹- or -OSiR¹⁰₂O-,

25

S¹ represents a direct bond, -O-, -S- or -NR⁹-,

p represents an integer from 2 to 12, preferably from 2 to 8, more preferably from 2 to 4,

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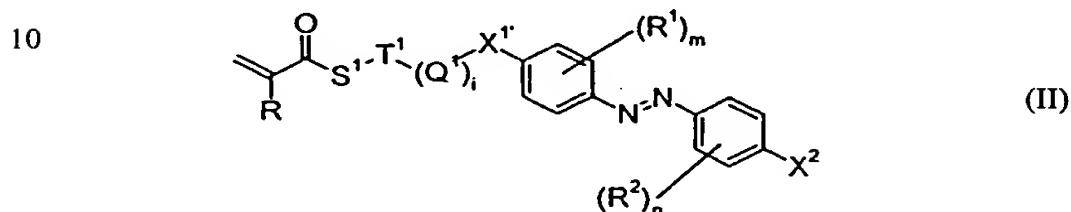
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R^9 represents hydrogen, methyl, ethyl or propyl,

R^{10} represents methyl or ethyl, and

5 R^5 to R^8 are as defined above.

Preferred dye monomers for polyacrylates or -methacrylates then have the formula (II)

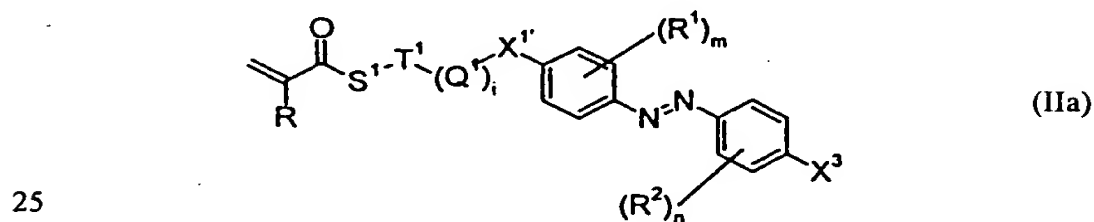


wherein

15 R represents hydrogen or methyl, and

the other radicals are as defined above.

20 Particularly suitable are dye monomers of the following formula (IIa)

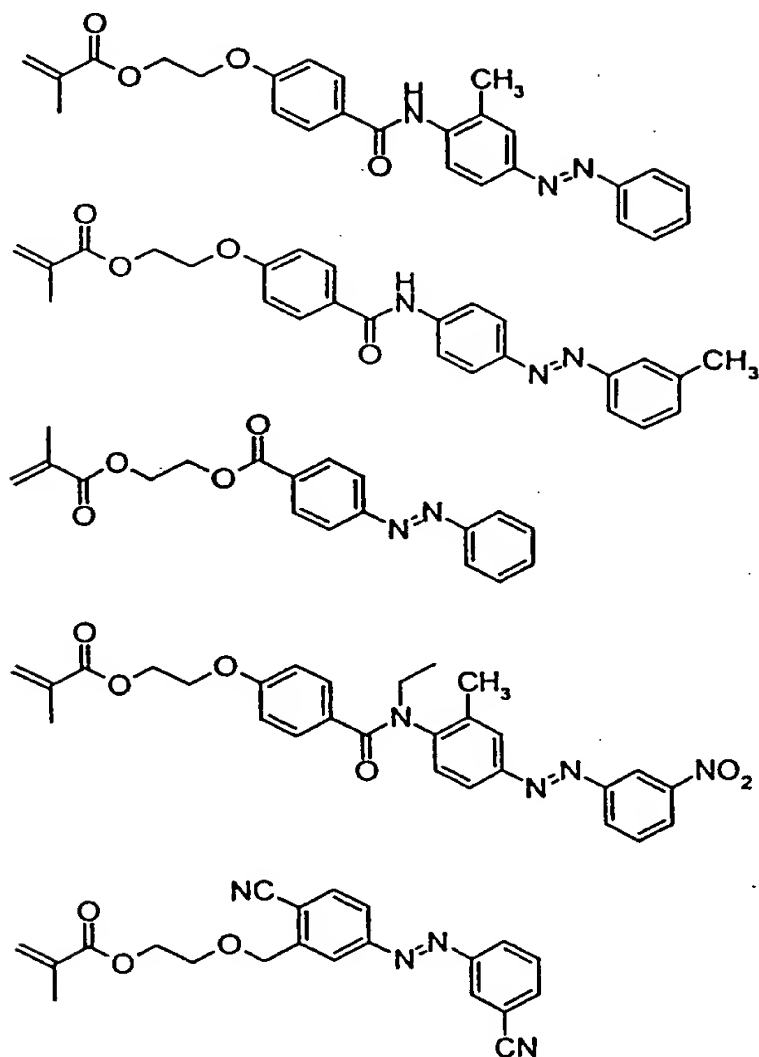


wherein

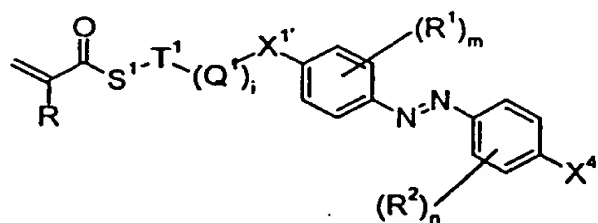
X^3 represents hydrogen, halogen or C_1 - to C_4 -alkyl, preferably hydrogen, and

30 the radicals R , S^1 , T^1 , Q^1 , X^1 , R^1 and R^2 and i , m and n are as defined above.

Particularly preferred monomers of formula (IIa) are, for example:



Also suitable are dye monomers of formula (IIb), when they are contained in the polymer in an amount of ≤ 10 mol%, preferably ≤ 5 mol%, more preferably ≤ 1 mol%,



(IIb),

- 12 -

wherein

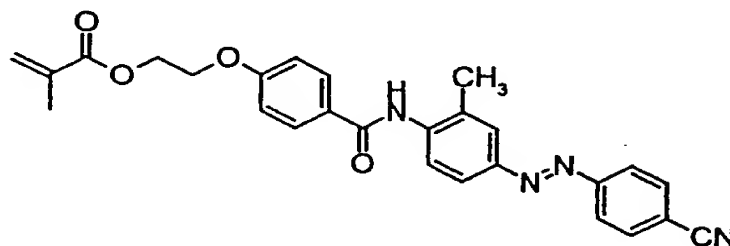
X⁴ represents cyano or nitro, and

5

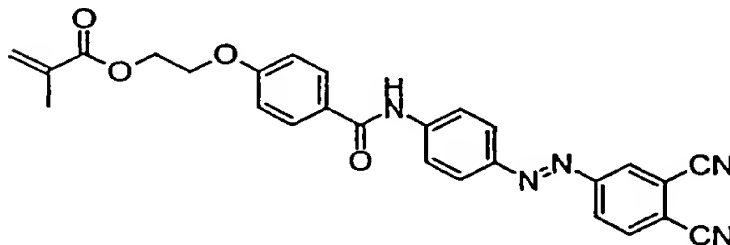
the radicals R, S¹, T¹, Q¹, X¹, R¹ and R² and i, m and n are as defined above.

Particularly preferred monomers of formula (IIb) are, for example,

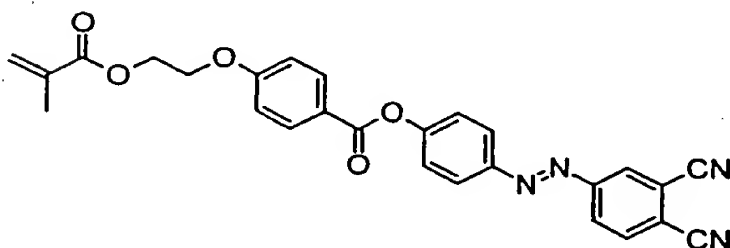
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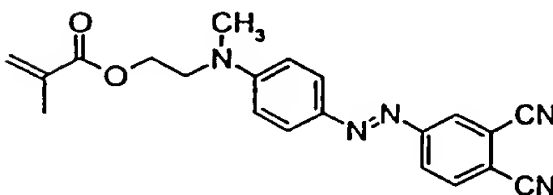
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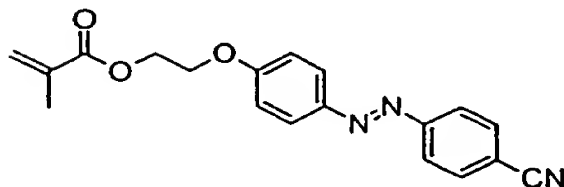
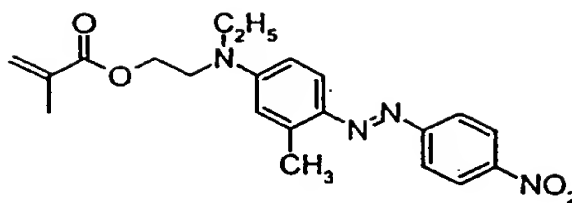
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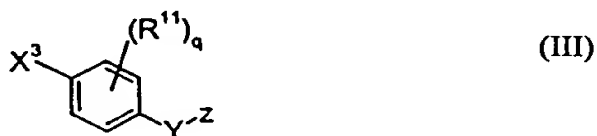
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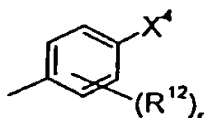


5 The polymeric or oligomeric organic, amorphous material according to the invention may carry in addition to the dyes, for example of formula (I), shape-anisotropic groupings. Those groupings, too, are generally bonded to the polymer structures covalently *via* a spacer.

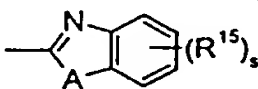
10 Shape-anisotropic groupings have, for example, the structure of formula (III)



20 wherein Z represents a radical of formula



(IIIa) or



(IIIb)

30 wherein

A represents O, S or N-C₁- to C₄-alkyl,

X³ represents -X^{3'}-(Q²)_j-T²-S²-,

X⁴ represents X^{4'}-R¹³,

X^{3'} and X^{4'} each independently of the other represents a direct bond, -O-, -S-,
 -(N-R⁵)-, -C(R⁶R⁷)-, -(C=O)-, -(CO-O)-, -(CO-NR⁵)-, -(SO₂)-, -(SO₂-O)-,
 -(SO₂-NR⁵)-, -(C=NR⁸)- or -(CNR⁸-NR⁵)-,

R⁵, R⁸ and R¹³ are each independently of the others hydrogen, C₁- to C₂₀-alkyl, C₃- to
 C₁₀-cycloalkyl, C₂- to C₂₀-alkenyl, C₆- to C₁₀-aryl, C₁- to C₂₀-alkyl-(C=O)-,
 C₃- to C₁₀-cycloalkyl-(C=O)-, C₂- to C₂₀-alkenyl-(C=O)-, C₆- to C₁₀-aryl-
 (C=O)-, C₁- to C₂₀-alkyl-(SO₂)-, C₃- to C₁₀-cycloalkyl-(SO₂)-, C₂- to C₂₀-
 alkenyl-(SO₂)- or C₆- to C₁₀-aryl-(SO₂)-, or

X^{4'}-R¹³ may represent hydrogen, halogen, cyano, nitro, CF₃ or CCl₃,

R⁶ and R⁷ each independently of the other represents hydrogen, halogen, C₁- to C₂₀-
 alkyl, C₁- to C₂₀-alkoxy, C₃- to C₁₀-cycloalkyl, C₂- to C₂₀-alkenyl or C₆- to
 C₁₀-aryl,

Y represents a single bond, -COO-, OCO-, -CONH-, -NHCO-, -CON(CH₃)-,
 -N(CH₃)CO-, -O-, -NH- or -N(CH₃)-,

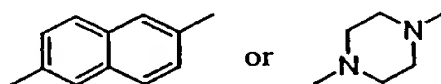
R¹¹, R¹², R¹⁵ each independently of the other represents hydrogen, halogen, cyano,
 nitro, C₁- to C₂₀-alkyl, C₁- to C₂₀-alkoxy, phenoxy, C₃- to C₁₀-cycloalkyl, C₂-
 to C₂₀-alkenyl or C₆- to C₁₀-aryl, C₁- to C₂₀-alkyl-(C=O)-, C₆- to C₁₀-aryl-

- 15 -

(C=O)-, C₁- to C₂₀-alkyl-(SO₂)-, C₁- to C₂₀-alkyl-(C=O)-O-, C₁- to C₂₀-alkyl-(C=O)-NH-, C₆- to C₁₀-aryl-(C=O)-NH-, C₁- to C₂₀-alkyl-O-(C=O)-, C₁- to C₂₀-alkyl-NH-(C=O)- or C₆- to C₁₀-aryl-NH-(C=O)-,

5 q, r and s each independently of the others represents an integer from 0 to 4, preferably from 0 to 2,

Q² represents -O-, -S-, -(N-R⁵)-, -C(R⁶R⁷)-, -(C=O)-, -(CO-O)-, -(CO-NR⁵)-, -
 10 -(SO₂)-, -(SO₂-O)-, -(SO₂-NR⁵)-, -(C=NR⁸)-, -(CNR⁸-NR⁵)-, -(CH₂)_p-, p- or m-C₆H₄- or a divalent radical of the formula



j represents an integer from 0 to 4, wherein when j > 1 the individual radicals
 15 Q¹ may have different meanings,

T² represents -(CH₂)_p-, wherein the chain may be interrupted by -O-, -NR⁹- or
 -OSiR¹⁰₂O-,

20 S² represents a direct bond, -O-, -S- or -NR⁹-,

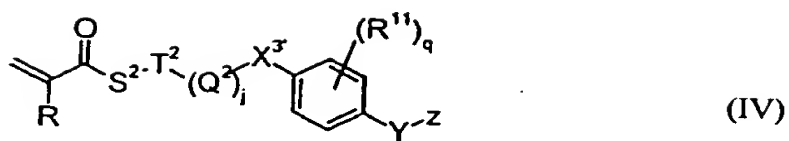
p represents an integer from 2 to 12, preferably from 2 to 8, more preferably
 from 2 to 4,

25 R⁹ represents hydrogen, methyl, ethyl or propyl, and

R¹⁰ represents methyl or ethyl.

Preferred monomers having such shape-anisotropic groupings for polyacrylates or
 30 -methacrylates then have the formula (IV)

- 16 -

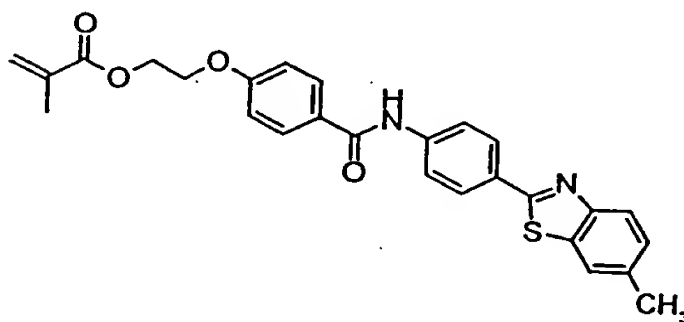
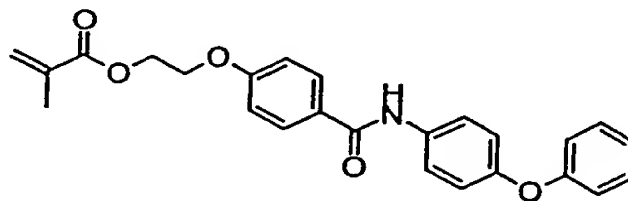
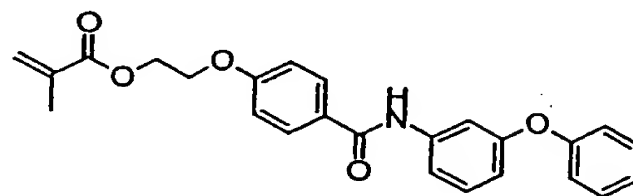


wherein

R represents hydrogen or methyl, and

the other radicals are as defined above.

Particularly preferred shape-anisotropic monomers of formula (IV) are, for example:



The alkyl, cycloalkyl, alkenyl and aryl radicals may in turn be substituted by up to three radicals from the group halogen, cyano, nitro, C₁- to C₂₀-alkyl, C₁- to C₂₀-

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- 17 -

alkoxy, C₃- to C₁₀-cycloalkyl, C₂- to C₂₀-alkenyl or C₆- to C₁₀-aryl, and the alkyl and alkenyl radicals may be straight-chained or branched.

Halogen is to be understood as being fluorine, chlorine, bromine and iodine, particularly fluorine and chlorine.

In addition to those functional units, the oligomers or polymers according to the invention may also contain units which serve mainly to lower the percentage content of functional units, especially of dye units. In addition to that function, they may also be responsible for other properties of the oligomers or polymers, for example the glass transition temperature, liquid crystallinity, film-forming property, etc..

For polyacrylates or -methacrylates, such monomers are acrylic or methacrylic acid esters of formula (V)



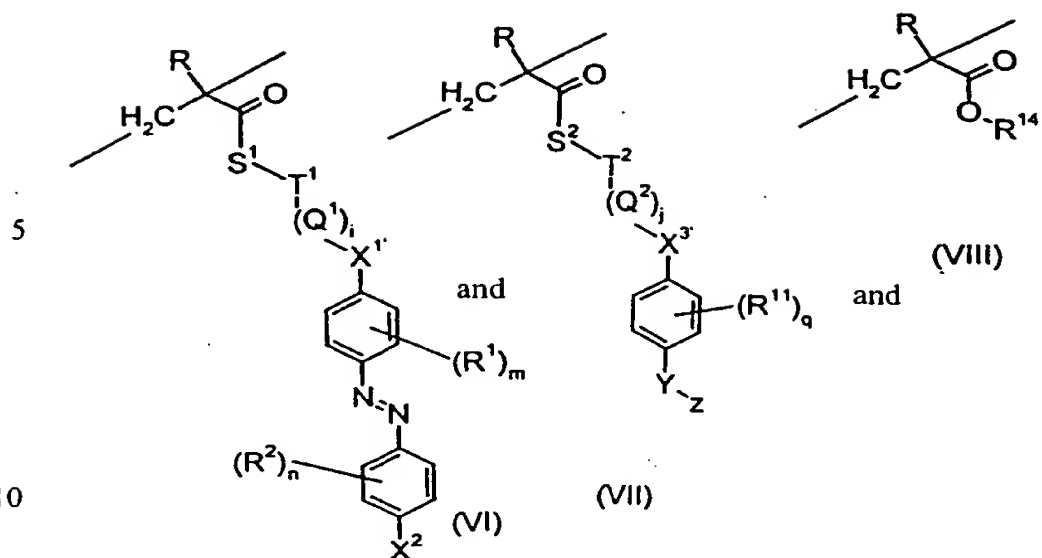
wherein

R represents hydrogen or methyl, and

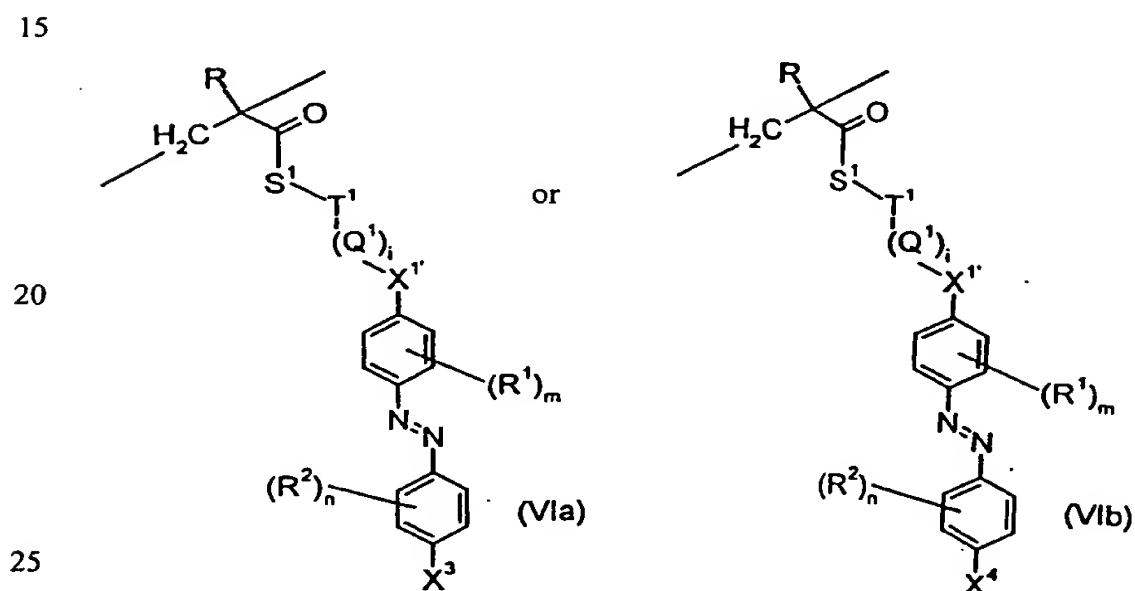
R¹⁴ represents optionally branched C₁- to C₂₀-alkyl or a radical containing at least one further acryl unit.

Polyacrylates and polymethacrylates according to the invention then contain as repeating units preferably those of formula (VI), preferably those of formulae (VI) and (VII) or of formulae (VI) and (VIII) or those of formulae (VI), (VII) and (VIII)

30



or, instead of formula (VI), repeating units of formula (VIa) or (VIb)



wherein the radicals are as defined above. It is also possible for there to be present several of the repeating units of formula (VI) ((VIa) or (VIb)) and/or of the repeating units of formula (VII) and/or (VIII).

5 The relative proportions of VI, (VIa, b), VII and VIII are as desired. The concentration of VI (VIa, b), depending on the absorption coefficient of VI (VIa, b), is preferably from 0.1 to 100 %, based on the mixture in question. The ratio of VI (VIa, b) to VII is from 100:0 to 1:99, preferably from 100:0 to 30:70, more preferably from 100:0 to 50:50.

The dyes of formula (I) and the dye monomers of formula (II) exhibit a principal absorption band (π - π^* band) in the short-wave range and a secondary absorption band (n - π^* band) in the longer wave range. The molar extinction coefficient ϵ of that n - π^* band is in the range of from 400 to $5000 \cdot 10^3$ cm²/mol. At an assumed dye molar mass of 400 g/mol, oligomers or polymers at an irradiated thickness of 0.1 mm have an optical density ≤ 2 , if they contain from ≤ 1.6 % (for $\epsilon = 5000$) to ≤ 20 % (for $\epsilon = 400$) of such dyes.

20 The polymers and oligomers according to the invention preferably have glass transition temperatures T_g of at least 40°C. The glass transition temperature can be determined, for example, according to B. Vollmer, Grundriß der Makromolekularen Chemie, p. 406-410, Springer-Verlag, Heidelberg 1962.

25 The polymers and oligomers according to the invention have a molecular weight, determined as the weight average, of from 5000 to 2,000,000, preferably from 8000 to 1,500,000, determined by gel permeation chromatography (calibrated with polystyrene).

Graft polymers are prepared by the free-radical binding of dye monomers of formula (II) or (IIa) or (IIb) and, optionally, additionally of shape-anisotropic monomers of

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formula (IV) and/or, optionally, additionally of monomers of formula (V) to oligomeric or polymeric base systems. Such base systems may be polymers of very different kinds, for example polystyrene, poly(meth)acrylates, starch, cellulose, peptides. The free-radical binding can be carried out by irradiation with light or by the use of reagents producing radicals, for example tert-butyl hydroperoxide, dibenzoyl peroxide, azodiisobutyronitrile, hydrogen peroxide/iron(II) salts.

As a result of the structure of the polymers and oligomers, the intermolecular interactions of the structural elements of formula (VI), (VIa, b) with one another or of formulae (VI), (VIa, b) and (VII) with one another are so adjusted that the formation of liquid-crystalline order states is suppressed and optically isotropic, transparent non-scattering films, foils, plates or cuboids can be produced. On the other hand, the intermolecular interactions are nevertheless sufficiently strong that, on irradiation with light, a photochemically induced, cooperative, directed reorientation process of the photochromic and non-photochromic side groups is brought about.

There preferably occur between the side groups of the repeating units of formula (VI), (VIa, b) or between those of formulae (VI), (VIa, b) and (VII) interaction forces which are sufficient for the photo-induced change in the configuration of the side groups of formula (VI), (VIa, b) to bring about a unidirectional - so-called cooperative - reorientation of the other side groups ((VI), (VIa, b) and/or (VII)).

In the optically isotropic amorphous photochromic polymers, extremely high values of the optical anisotropy can be induced (Δn to 0.4).

As a result of the influence of actinic light, order states in the polymers or oligomers are generated and modified and the optical properties are thus modulated.

The light used is polarised light whose wavelength lies in the range of the absorption band, preferably in the range of the long-wave $n-\pi^*$ band, of the repeating units of formula (VI).

5 The polymers and oligomers can be prepared by processes known in the literature, for example in accordance with DD 276 297, DE-A 3 808 430, Makromolekulare Chemie **187**, 1327-1334 (1984), SU 887 574, Europ. Polym. **18**, 561 (1982) and Liq. Cryst. **2**, 195 (1987).

10 The preparation of films, foils, plates and cuboids is possible without the necessity
for complex orientation processes using external fields and/or surface effects. They
can be applied to substrates by spin coating, immersion, pouring or other coating
processes which are readily controllable from a technological point of view, can be
brought between two transparent plates by pressing or flowing, or can simply be
15 prepared as a self-supporting material by pouring or extrusion. Such films, foils,
plates and cuboids can also be prepared from liquid-crystalline polymers or
oligomers which contain structural elements in the described sense, by sudden
cooling, that is to say by a cooling rate of $> 100 \text{ K/min.}$, or by rapid removal of the
solvent.

20

Preference is given to a process for preparing the holographic volume storage medium in which there is contained a step according to a conventional injection-moulding process in the range up to 300°C, preferably up to 220°C, more preferably 180°C.

The layer thickness is ≥ 0.1 mm, preferably ≥ 0.5 mm, more preferably ≥ 1 mm. An especially preferred preparation process for layers in the millimetre range is the injection-moulding process. In that process, the polymer melt is forced through a nozzle into a shaping holder, from which it can be removed after cooling.

- 22 -

A preferred method of preparing the recording material or the polymer according to the invention contains a process wherein at least one monomer is polymerised without further solvent, the polymerisation preferably being free-radical polymerisation and, more preferably, being initiated by free-radical initiators and/or UV light and/or thermally.

The process is carried out at temperatures of from 20°C to 200°C, preferably from 40°C to 150°C, more preferably from 50°C to 100°C and most preferably of about 60°C.

In a particular embodiment, AIBN is used as the free-radical initiator.

It has frequently been found to be advantageous to use concomitantly a further, preferably liquid monomer. Such monomers are to be understood as being monomers which are liquid at the reaction temperatures, which monomers are preferably olefinically unsaturated monomers, more preferably based on acrylic acid and methacrylic acid, most preferably methyl methacrylate.

The content of monomers of formula (II) in the copolymers is preferably from 0.1 to 99.9 wt.%, more preferably from 0.1 to 50 wt.%, more preferably still from 0.1 to 5 wt.% and, most preferably, from 0.5 to 2 wt.%.

The method of holographic data storage is described, for example, in LASER FOCUS WORLD, NOVEMBER 1996, page 81 ff.

On recording a hologram, the above-described polymer films are irradiated by two coherent laser beams of a wavelength that brings about the required light-induced reorientations. One beam, the object beam, contains the optical information to be stored, for example the variation in intensity resulting from the passage of a light beam through a two-dimensional, chequered pixel structure (data page). In principle,

- 23 -

however, light that is diffracted, scattered or reflected by any two- or three-dimensional object can be used as the object beam. On the storage medium, the object beam is brought to interference with the second laser beam, the reference beam, which is generally a flat or circular wave. The resulting interference pattern is imprinted in the storage medium as modulation of the optical constants (refractive index and/or absorption coefficient). That modulation permeates the entire irradiated area, especially the thickness of the storage medium. If the object beam is then blocked off and the medium is exposed solely to the reference beam, the modulated storage medium acts as a kind of diffraction grating for the reference beam. The intensity distribution resulting from the diffraction corresponds to the intensity distribution which originated from the object to be stored, so that it is no longer possible to distinguish whether the light comes from the object itself or whether it results on account of diffraction of the reference beam.

For the storing of different holograms at one specimen position, various multiplex processes are used: wavelength multiplexing, shift multiplexing, phase multiplexing, peristrophic multiplexing and/or angle multiplexing and/or others. In the case of angle multiplexing, the angle between the storage medium, in which a hologram has been stored under the relevant angles, and the reference beam is changed. From a certain angle change, the original hologram disappears (Bragg mismatch): the incident reference beam can no longer be deflected by the storage medium to reconstruct the object. The angle from which that occurs depends on the thickness of the storage medium (and on the modulation of the optical constants produced in the medium): the thicker the medium, the smaller the angle by which the reference beam must be changed.

A further hologram can be recorded in that new angle configuration. The reading of that hologram again takes place precisely in the angle configuration between the storage medium and the reference beam in which it was recorded.

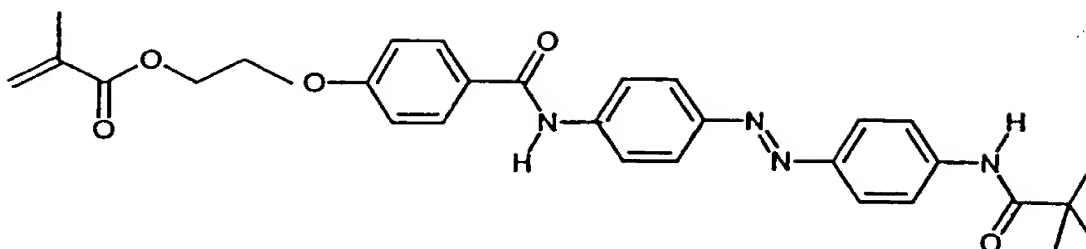
By gradually changing the angle between the medium and the recording beams, it is therefore possible to record a plurality of holograms in the same place on the storage medium.

5 The polymer systems described in the present patent have the great advantage that, when a subsequent hologram is recorded, the information deposited in the storage medium relating to the previous holograms is not erased and that more than three
10 holograms, preferably more than 50, more preferably more than 100, more preferably still more than 500 and most preferably more than 1000 holograms can be recorded at one place on the storage medium. The objects to be stored are data pages produced by transmission of a liquid crystal display. Those data pages have 256 x 256 pixels, preferably 512 x 512 pixels, preferably 1024 x 1024 data pixels.

15 The invention also provides a recording material for a holographic volume storage medium consisting of a polymeric or oligomeric organic, amorphous material which contains at least one grouping that interacts with electromagnetic radiation and, optionally, at least one shape-anisotropic grouping, characterised in that it has an optical density ≤ 2 , preferably ≤ 1 , more preferably ≤ 0.3 . The recording material can be used for storing data in the form of an unsupported film or, preferably, in a
20 multilayer structure. The multilayer structure is, for example, a sandwich in which the actual recording medium is surrounded by at least one substrate. The substrate may be transparent media having high optical quality, for example glass plates, quartz plates or plates of polycarbonate. High optical quality is to be understood as meaning that the scattering efficiency, that is to say the quotient between light
25 scattered at that sandwich and the incident light, is not less than 10^{-4} , preferably not less than 10^{-5} , more preferably not less than 10^{-6} . In order to determine that quotient, the sample can be exposed to the beam of an HeNe laser. Detection is by means of a CCD camera.

Examples:**Example 1**

5 Preparation of monomers:

a) *4-(2-Hydroxyethoxy)benzoic acid*

138 g of p-hydroxybenzoic acid and 0.5 g of KI are placed in 350 ml of ethanol, with stirring. A solution of 150 g of KOH in 150 ml of water is added dropwise. 88.6 g of ethylenechlorohydrin are added dropwise at 30-60°C in the course of 30 minutes. The reaction mixture is stirred under reflux for 15 hours. The solvent is then distilled off completely first under normal pressure and then *in vacuo*. The residue is dissolved in 1 litre of water and acidified using HCl. The precipitate is filtered off with suction and recrystallised from 1.8 litres of water. The product is dried and recrystallised twice from ethanol. The yield is 46 g (25 % of the theoretical yield). M.p. 179.5°C.

b) *4-(2-Methacryloyloxyethoxy)benzoic acid*

45 g of 4-(2-hydroxyethoxy)benzoic acid, 180 ml of methacrylic acid, 10 g of p-toluenesulfonic acid and 10 g of hydroquinone are heated at reflux in 150 ml of chloroform, with stirring. The water that forms during the reaction is separated off in a water separator. The reaction mixture is diluted with 150 ml of chloroform, washed several times using 100 ml of water each time, and dried over Na₂SO₄. The drying agent is filtered off and the chloroform is distilled off to two thirds in a rotary evaporator. The product precipitates, is

- 26 -

filtered off with suction and is recrystallised twice from isopropanol. The yield is 28 g (45 % of the theoretical yield). M.p. 146°C.

c) *4-(2-Methacryloyloxyethyloxy)benzoic acid chloride*

25 g of 4-(2-methacryloyloxyethyloxy)benzoic acid, 80 ml of thionyl chloride and 0.5 ml of DMF are stirred at room temperature for 30 minutes. Excess thionyl chloride is then distilled off first under a moderate vacuum and then under a high vacuum. The acid chloride formed in a virtually quantitative yield then slowly crystallises out at room temperature.

Elemental analysis: $C_{13}H_{13}ClO_4$ (268.7)

calc.: C 58.11; H 4.88; Cl 13.19;

found: C 58.00; H 4.90; Cl 13.20.

d) *4-Pivalinoylamino-4'-aminoazobenzene*

36 g of 4,4'-diaminoazobenzene and 62 g of triethylamine are placed in 400 ml of THF. A solution of 23.2 g of pivalic acid chloride in 100 ml of THF is slowly added dropwise. After 2 hours' stirring at room temperature, water is added to the reaction mixture. The precipitate is filtered off and dried. 42 g of the product are obtained. Further purification is carried out by chromatography (silica gel; toluene/ethyl acetate 1:1). The yield is 8 g. M.p. 230°C.

e) *4-Pivalinoylamino-4'-[p-(2-methacryloyloxy-ethyloxy)benzoylamino]azobenzene*

1 g of 4-pivalinoylamino-4'-aminoazobenzene is placed in 10 ml of N-methyl-2-pyrrolidone (NMP) at 50°C and added to a solution of 1 g of 4-(2-methacryloyloxyethyloxy)benzoic acid in 1 ml of NMP at 50°C. The reaction mixture is stirred at that temperature for one hour and is cooled, and 200 ml of water are added. The precipitate is filtered off and stirred in 30 ml of

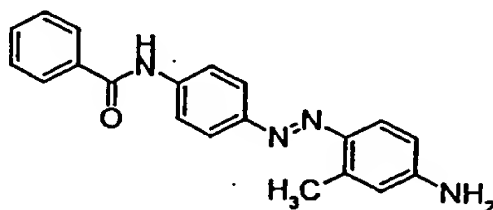
- 27 -

methanol at room temperature; the mother liquor is filtered off and drying is carried out *in vacuo*. The yield is 1.2 g. M.p. 194°C. $\lambda_{\max} = 378 \text{ nm}$ (DMF); $\epsilon = 37000 \text{ l/(mol*cm)}$.

5 Example 2

a) 32 g of N-benzoyl-p-phenylenediamine were placed in a mixture of 210 ml of glacial acetic acid, 75 ml of propionic acid and 31 ml of concentrated hydrochloric acid at 3-5°C. 50 g of nitrosylsulfuric acid (approx. 40 %) were added dropwise at that temperature over a period of one hour.

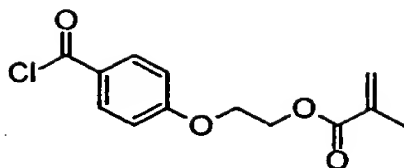
b) 16 g of m-toluidine were dissolved in 130 ml of glacial acetic acid. At 0-5°C, the diazotisation from a) was added dropwise thereto over a period of 2 hours. The mixture was stirred overnight at room temperature. The resulting dye was filtered off with suction and suspended in 550 ml of water. The pH was raised to 8.4 using soda. The dye was filtered off with suction again, washed with isopropanol and dried. 27 g (54.4 % of the theoretical yield) of the dye of the formula



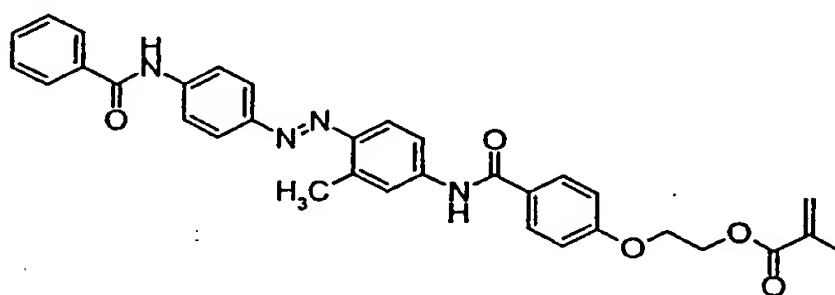
were obtained. UV/VIS in dimethylformamide: $\lambda_{\max} = 416 \text{ nm}$.

c) 5 g of the dye from b) were dissolved in 20 ml of N-methylpyrrolidone at 50°C. 3.5 g of the acid chloride of the formula

- 28 -

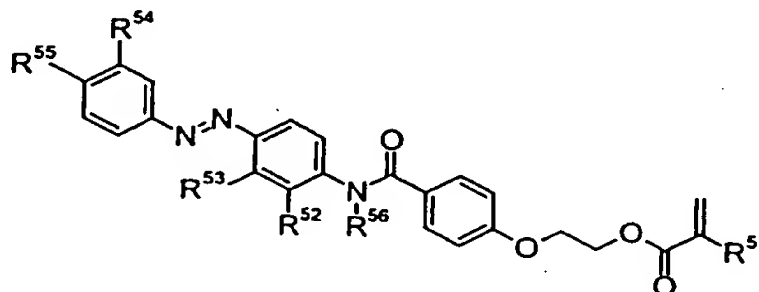


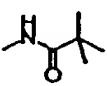
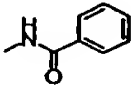
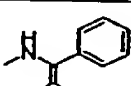
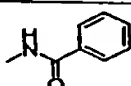
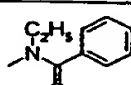
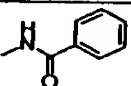
were added. The mixture was stirred for 1.5 hours at 50°C. Finally, 20 ml of water were added and the resulting dye was filtered off with suction. It was stirred with 50 ml of isopropanol, filtered off with suction and dried. 6.2 g (73.4 % of the theoretical yield) of the dye monomer of the formula



were obtained. UV/VIS in dimethylformamide: $\lambda_{\max} = 386 \text{ nm}$.

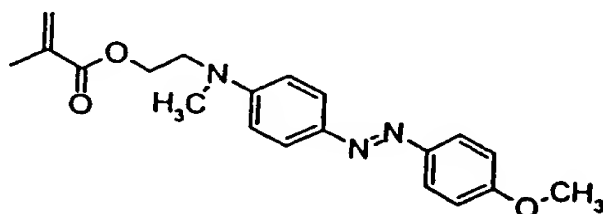
The dye monomers of the following Table were prepared analogously.



Example	R ⁵¹	R ⁵²	R ⁵³	R ⁵⁴	R ⁵⁵	R ⁵⁶	λ_{\max}
2	CH ₃	H	H	H		H	
3	CH ₃	CH ₃	H	H		H	374 nm
4	H	H	CH ₃	H		H	386 nm
5	CH ₃	CH ₃	H	H		C ₂ H ₅	371 nm
6	CH ₃	H	CH ₃	H		H	395 nm
7	CH ₃	H	CH ₃		CH ₃	H	373 nm

Example of graft polymers

8.7 g of the starch Perfectamyl A 4692 (86.3 %) from Avebe, Foxhol, NL, were dissolved in 60 ml of water at 86°C. A mixture of 1.5 g of a 1 wt.% aqueous FeSO₄ solution and 6.1 g of a 3 wt.% aqueous H₂O₂ solution were added thereto. Stirring was carried out for 15 minutes at 86°C. Then, at that temperature, a solution of 1.4 g of the dye monomer of the formula



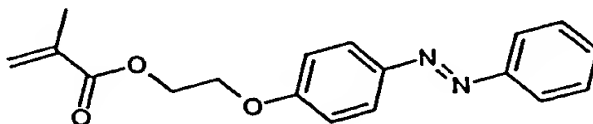
- 30 -

in 12.5 g of methyl methacrylate and 4.1 g of a 3 wt.% aqueous H_2O_2 solution were simultaneously added dropwise over a period of 90 minutes. After a further 15 minutes at that temperature, 0.105 g of tert-butyl hydroperoxide was added and stirring was carried out for a further one hour at 86°C. The fine yellow dispersion was filtered through a 100 μ m polyamide filter.

The dispersion was diluted 1:10 with water, applied to a glass plate and dried. The transparent pale yellow film on the glass plate was irradiated for 10 minutes with polarised light, KL 500 cold light lamp from Schott (spot diameter 6 mm). Between crossed polarisers, the irradiated spot could be seen brightly in dark surroundings.

Example 3: Preparation of holographic materials by block polymerisation

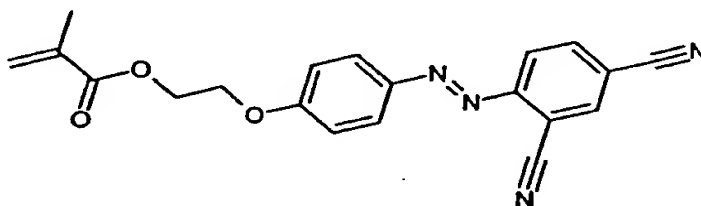
A solution of 0.314 g of 4-(2-methacryloyloxyethoxy)azobenzene (1 mol%)



and 0.052 g of 2,2'-azoisobutyric acid nitrile in 10 g of methyl methacrylate was rinsed with dry argon in a glass ampoule for 30 minutes. The ampoule was closed with a rubber stopper and tempered for 7 days at 60°C. A transparent polymer cylinder was obtained. The polymer cylinder could be isolated by breaking the ampoule and removing the broken glass. Further storage for 2 weeks at 60°C served to remove the methyl methacrylate residues and relieve the stresses within the polymer block.

The PAP cylinder so obtained was cut into plates having a diameter of 17 mm and a thickness of 1.9 mm in a precision engineering workshop and was then polished. The plates have the following optical densities at the important wavelengths: OD(514 nm) = 2.502; OD(532 nm) = 0.755; OD(568 nm) = 0.052.

In an analogous manner, copolymer having an azo dye content of 10 mol% is prepared. In an analogous manner, copolymer is prepared having a content of the monomer:



of 1 mol% and a methyl methacrylate content of 99 mol%.

Example 4

The polymer from Example 3 is applied to a glass substrate having a thickness of 150 μm by means of spin coating from a solution. The layer thickness of the measuring point located at the centre of the substrate is 600 nm. The level of the refractive index n of the polymer layer is determined for the three spatial directions x , y (layer plane) and z (layer normal) by the prism coupling method. To that end, the base of a prism is brought into close contact with the polymer layer. The angles at which the polarised light of a laser couples into the layer and passes through it in the manner of a waveguide give information about its refractive index at the wavelength of light. Each coupling in becomes clear as a signal drop on a detector in reflection.

When the polarisation of the laser is chosen perpendicular to the incident plane (s-polarisation), the refractive index in the polarisation direction can be determined. According to the orientation of the substrate, the values for n_x and n_y can be determined. The index of the substrate which has the lower refractive index, the index of the prism and the laser wavelength ($\lambda = 633$ nm) enter into the calculations. In the case of polarisation in the incident plane (p-polarisation), the value for n_z can be determined. To that end, one of the two spatial directions x or y must coincide with the incident plane. Additionally, the value of the refractive index of the direction so chosen (n_x or n_y) enters into the calculation.

The refractive indices n_x , n_y and n_z are determined on the sample before, during and after several exposures and cancellation processes. Exposure is effected by irradiating the polymer layer with laser light of wavelength $\lambda = 514$ nm in perpendicular incidence. The light intensity is 200 mW/cm². The light is polarised linearly in the x direction. Cancellation of the orientation anisotropy so induced in the xy plane takes place on polarisation in the y direction.

Sample	Refractive index at $\lambda = 633$ nm		
	n_x	n_y	n_z
Untreated	1.692	1.692	1.657
After 200 seconds' exposure	1.657	1.721	1.682
After 500 seconds' exposure	1.626	1.732	1.700
After 5000 seconds' exposure	1.596	1.746	1.716
After 1st cancellation	1.672	1.675	1.723
After 2nd exposure (5000 s)	1.588	1.721	1.730
After 2nd cancellation	1.650	1.651	1.735

The level of the refractive index of each spatial direction is a measure of the mean number of chromophores oriented in that direction, because it correlates with the

inducible polarisation and that is composed principally of the high molecular polarisabilities along each molecular axis. Since n_x and n_y are originally identical, there is a macroscopically isotropic distribution in the xy plane. The smaller value for n_z indicates the planar molecular orientation, resulting from the preparation process. The first exposure leads gradually to an orientation distribution with a reduced number of chromophores lying in the x direction. The depletion in that direction takes place in the statistical mean in equal parts in favour of the other two spatial directions y and z, to be read off from the increasing values of n_y and n_z . A double refraction $n_y - n_x$ in the film plane can be cancelled again almost completely. The number of chromophores oriented in the z direction increases, however, with each further exposure or cancellation procedure.

Example 5

The polymer from Example 3 is present in the form of a granulate. It is applied to a glass substrate and heated to approximately 180°C. At that temperature, the polymer melts. On the glass substrate there are located spacers, for example of mylar film or glass fibres, and a further cover glass. Using that glass-polymer-glass sandwich, layers in the range of from 20 to 1000 μm are produced.

Example 6

A 500 μm thick polymer film, prepared by the process of Example 5, is studied in a holographic structure. An SHG Nd:YAG laser (532 nm) is used as the recording source. In the beam path of the object beam there lies a Spatial Light Modulator, which produces a data mask of 1024 x 1024 pixels. The intensity ratio of the reference beam to the object beam is 7:1, the total power density falling on the sample is 200 mW/cm². A hologram is recorded by superposing the reference beam and the object beam, which are polarised perpendicularly to the incident planes and which fall onto the sample at an angle of 40° relative to each other and expose the

- 34 -

sample for 30 seconds; the hologram is subsequently read out by exposure solely with the reference beam (exposure time 10 milliseconds). By changing the angle of the reference beam by 0.25° , the Bragg condition is broken and the original hologram is no longer visible. A new hologram is recorded under that new angle configuration. The process is repeated 100 times. After each recording process, there are read out in addition to the hologram just recorded also all previously recorded holograms by adjusting the corresponding reference angle. Even after completion of the 100 recording processes, the information in all the holograms is retained.

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